## **Supplementary Information**

## Atomic-scale regulation of anionic and cationic migration in alkali metal batteries

Pan Xiong<sup>1,2,#</sup>, Fan Zhang<sup>2,#</sup>, Xiuyun Zhang<sup>3,#</sup>, Yifan Liu<sup>1</sup>, Yunyan Wu<sup>1</sup>, Shijian Wang<sup>2</sup>, Javad Safaei<sup>2</sup>, Bing Sun<sup>2</sup>, Renzhi Ma<sup>4</sup>, Zongwen Liu<sup>5</sup>, Yoshio Bando<sup>4</sup>, Takayoshi Sasaki<sup>4</sup>, Xin Wang<sup>1</sup>, Junwu Zhu<sup>1\*</sup>, Guoxiu Wang<sup>2\*</sup>

<sup>1</sup>Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, Nanjing, 210094, China

<sup>2</sup>Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, University of Technology Sydney, NSW 2007, Australia

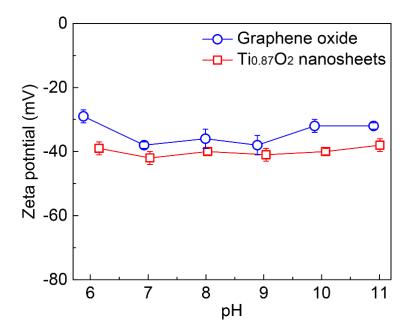
<sup>3</sup>College of Physical Science and Technology, Yangzhou University, Yangzhou, 225002, China

<sup>4</sup>International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

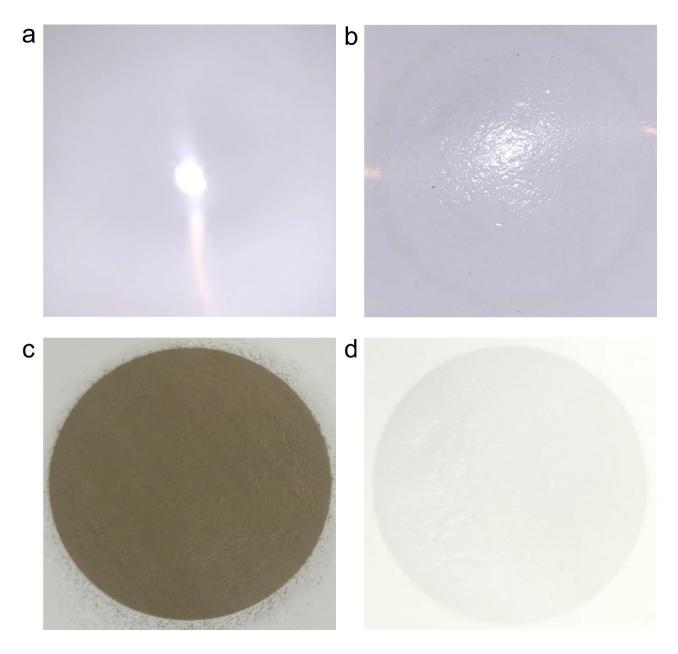
<sup>5</sup>School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

\*These authors contributed equally: Pan Xiong, Fan Zhang, Xiuyun Zhang

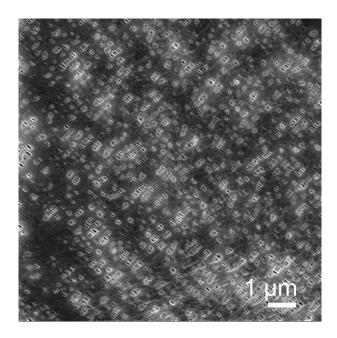
<sup>\*</sup>e-mail: zhujw@njust.edu.cn; guoxiu.wang@uts.edu.au



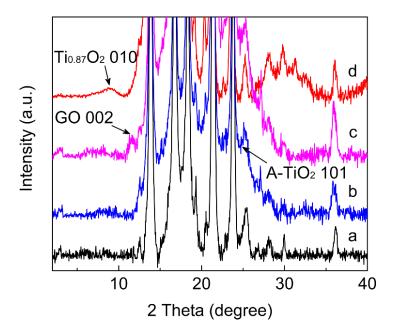
Supplementary Figure 1. Zeta-potentials of the suspensions of graphene oxide and  $Ti_{0.87}O_2$  nanosheets.



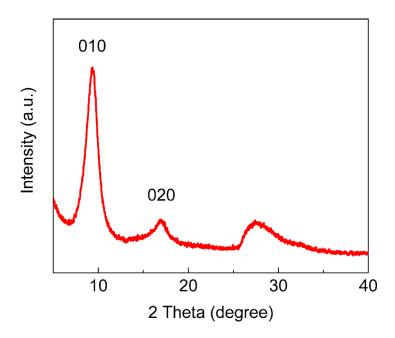
Supplementary Figure 2. Photographs of the (a) PP, (b) anatase  $TiO_2/PP$ , (c) GO/PP, and (d)  $Ti_{0.87}O_2/PP$  separators.



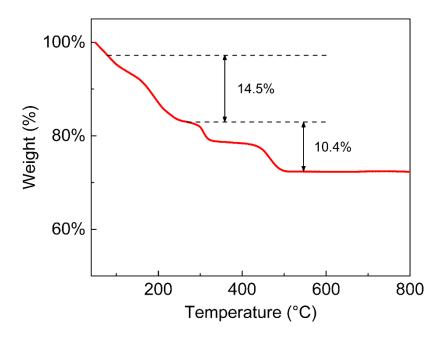
**Supplementary Figure 3.** SEM image of the commercial PP separators.



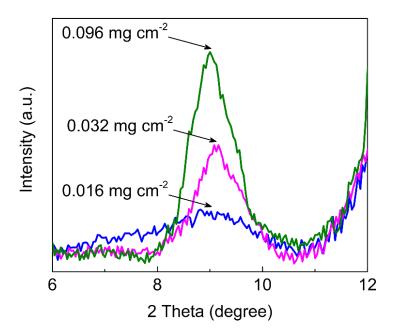
**Supplementary Figure 4.** XRD patterns of (a) PP, (b) anatase TiO<sub>2</sub>/PP, (c) GO/PP, and (d) Ti<sub>0.87</sub>O<sub>2</sub>/PP separators. The 101 diffraction peak of anatase TiO<sub>2</sub> (A-TiO<sub>2</sub>), 002 diffraction peak of GO and 010 diffraction peak of Ti<sub>0.87</sub>O<sub>2</sub> were marked.



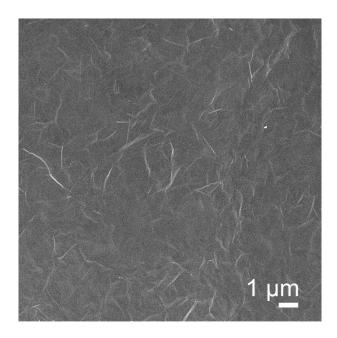
Supplementary Figure 5. XRD pattern for the Ti<sub>0.87</sub>O<sub>2</sub> nanosheets without PP separators.



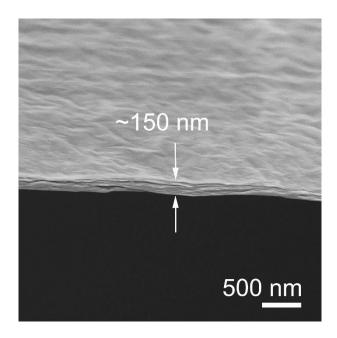
**Supplementary Figure 6.** Thermogravimetric curve for the nanosheet films without PP separators.



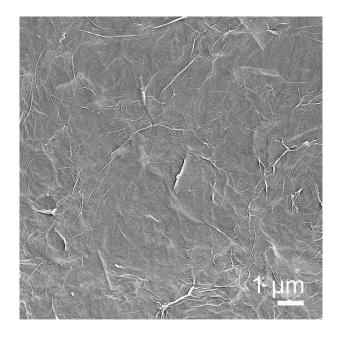
**Supplementary Figure 7.** XRD patterns of Ti<sub>0.87</sub>O<sub>2</sub>/PP separators with different surface area mass loadings.



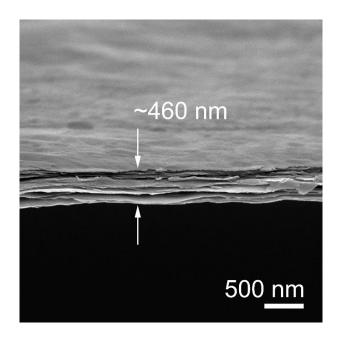
Supplementary Figure 8. SEM image of  $Ti_{0.87}O_2/PP$  separators with a surface area mass loading of  $0.032~mg~cm^{-2}$ .



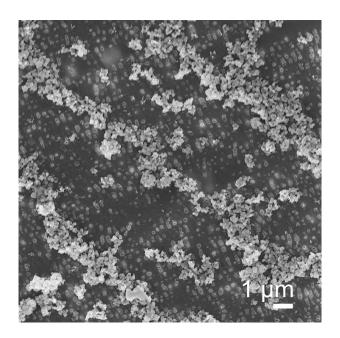
Supplementary Figure 9. Cross-section SEM image of  $Ti_{0.87}O_2/PP$  separators with a surface area mass loading of  $0.032~mg~cm^{-2}$ .



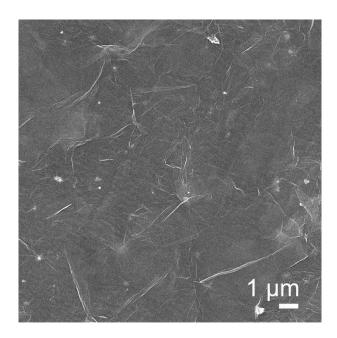
Supplementary Figure 10. SEM image of  $Ti_{0.87}O_2/PP$  separators with a surface area mass loading of  $0.096~mg~cm^{-2}$ .



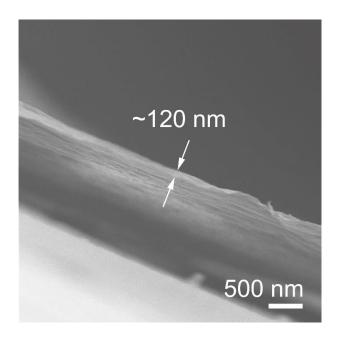
Supplementary Figure 11. Cross-section SEM image of  $Ti_{0.87}O_2/PP$  separators with a surface area mass loading of 0.096 mg cm<sup>-2</sup>.



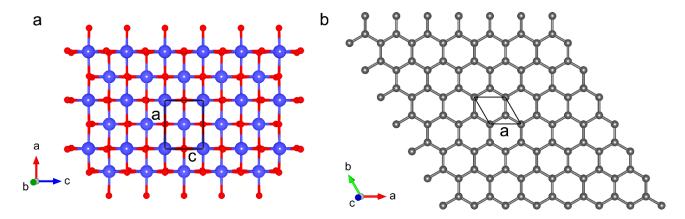
Supplementary Figure 12. SEM image of anatase  $TiO_2/PP$  separators with a surface area mass loading of 0.016 mg cm<sup>-2</sup>.



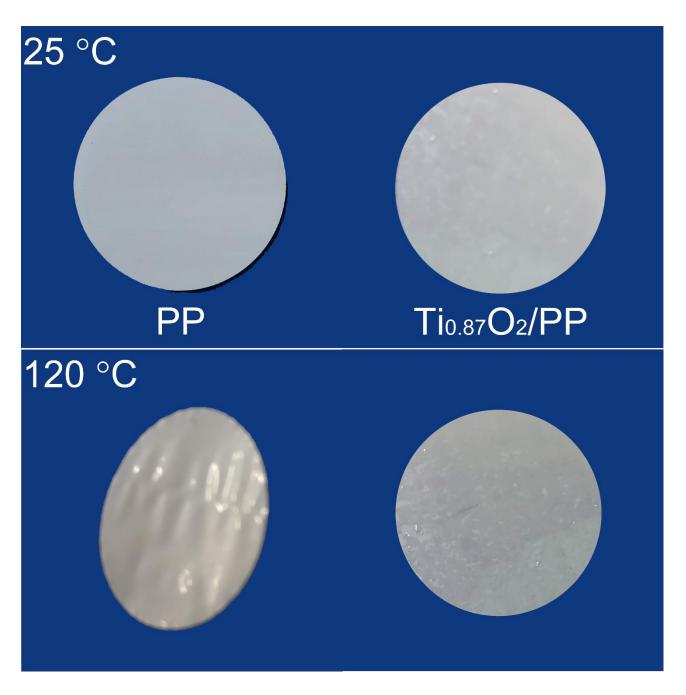
**Supplementary Figure 13.** SEM image of GO/PP separators with a surface area mass loading of 0.016 mg cm<sup>-2</sup>.



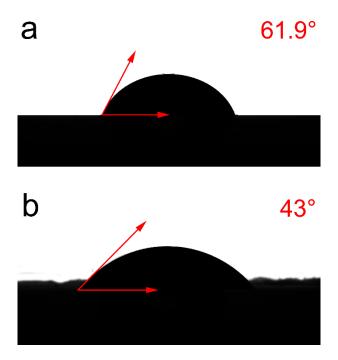
**Supplementary Figure 14.** Cross-section SEM image of GO/PP separators with a surface area mass loading of  $0.016~\rm mg~cm^{-2}$ .



Supplementary Figure 15. 2D theoretical specific surface area of Ti<sub>0.87</sub>O<sub>2</sub> and GO monolayers. (a) In-plane structure of Ti<sub>0.87</sub>O<sub>2</sub> with a rectangular unit cell: a = 0.38 nm and c = 0.30 nm. (b) In-plane structure of graphene with a hexagonal unit cell: a = 0.25 nm. The ideal graphene structure was used to estimate the 2D theoretical specific surface area of GO. For an approximate calculation, the single layers of Ti<sub>0.87</sub>O<sub>2</sub> and graphene were assumed to neatly deposit on the PP separator without gap. The 2D theoretical specific surface area of Ti<sub>0.87</sub>O<sub>2</sub> single layer can be calculated based on the in-plane unit cell area,  $W_{\text{(Ti<sub>0.87</sub>O<sub>2)}} = 2 M_{\text{(Ti<sub>0.87</sub>O<sub>2)}} / (a \times c \times N_{\text{A}})$ . The 2D theoretical specific surface area of GO single layer can be calculated based on the in-plane unit cell area,  $W_{\text{(GO)}} = 2 M_{\text{(C)}} / (a \times a \times \sin 120^{\circ} \times N_{\text{A}})$ .  $N_{\text{A}}$  is the Avogadro's number,  $M_{\text{(Ti<sub>0.87</sub>O<sub>2)}}$  and  $M_{\text{(C)}}$  are the formula weights of Ti<sub>0.87</sub>O<sub>2</sub> and carbon. Under a same specific surface area,  $W_{\text{(GO)}} \times n_{\text{(GO)}} = W_{\text{(Ti<sub>0.87</sub>O<sub>2)}} \times n_{\text{(Ti<sub>0.87</sub>O<sub>2)}}$ .  $n_{\text{(GO)}}$  and  $n_{\text{(Ti<sub>0.87</sub>O<sub>2)}}$  are the number of single layers of GO and Ti<sub>0.87</sub>O<sub>2</sub>, respectively. So, the  $n_{\text{(GO)}} / n_{\text{(Ti<sub>0.87</sub>O<sub>2)}} = \sim 2.9$ . Considering the crystallinity thickness of GO and Ti<sub>0.87</sub>O<sub>2</sub> with the same specific surface area is  $h_{\text{(GO)}} / h_{\text{(Ti<sub>0.87</sub>O<sub>2)}} = \sim 1.36$ .</sub></sub></sub></sub></sub></sub></sub></sub>



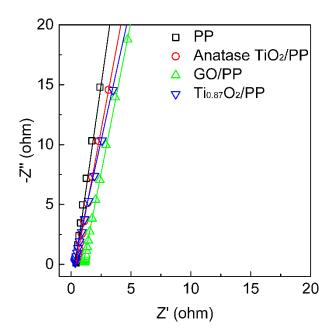
**Supplementary Figure 16.** Photographic pictures of the PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators before and after heating process.



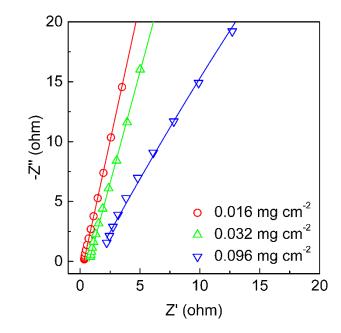
Supplementary Figure 17. Contact angle measurements for electrolytes (1 M LiTFSI in DME: DOL 1: 1, v/v) on (a) PP and (b)  $Ti_{0.87}O_2/PP$  separators.



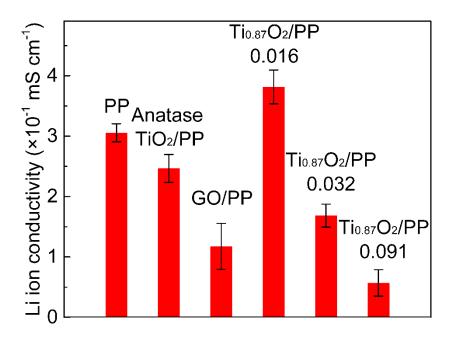
**Supplementary Figure 18.** Digital photos of the Ti<sub>0.87</sub>O<sub>2</sub>/PP separator under different bending conditions.



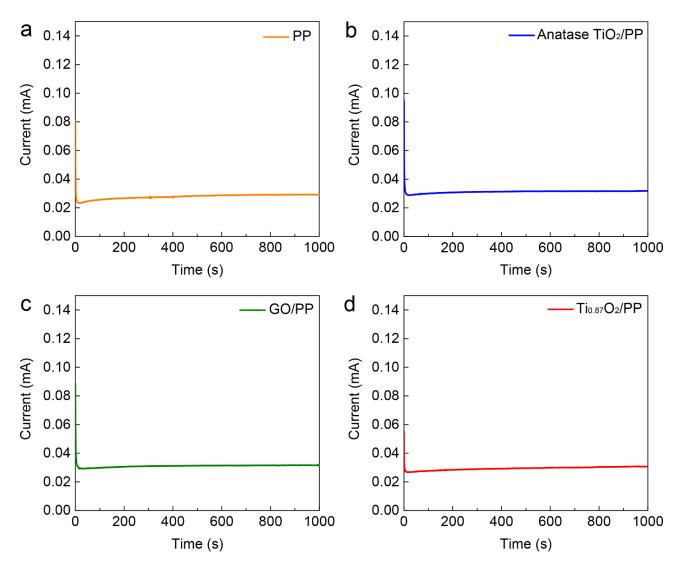
**Supplementary Figure 19.** Nyquist plots of PP, anatase TiO<sub>2</sub>/PP, GO/PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators estimating the Li-ion conductivity.



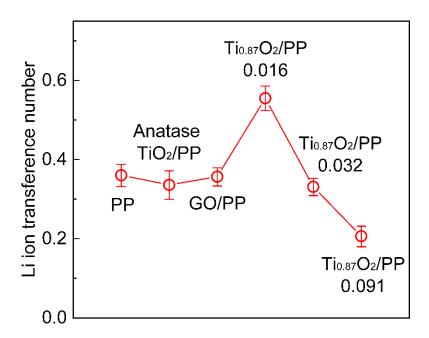
Supplementary Figure 20. Nyquist plots of Ti<sub>0.87</sub>O<sub>2</sub>/PP separators with different weight densities.



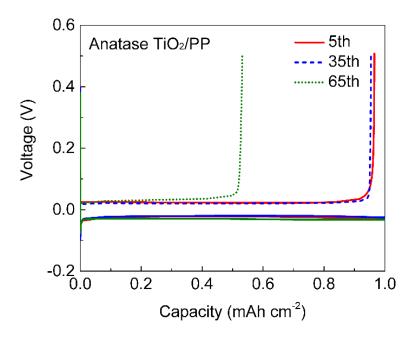
**Supplementary Figure 21.** Li ion conductivity of PP, anatase TiO<sub>2</sub>/PP, GO/PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators with different surface area mass loadings. Error bars were included, which represent the standard deviation of the data taken from five samples.



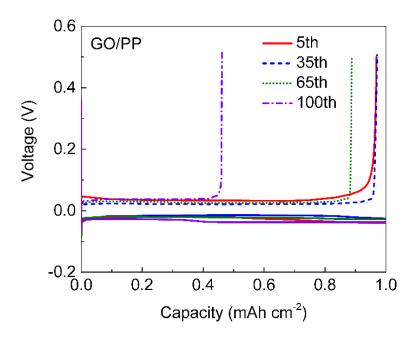
**Supplementary Figure 22.** Chronoamperometric measurements of PP, anatase TiO<sub>2</sub>/PP, GO/PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators.



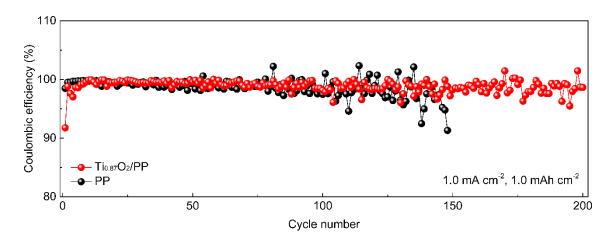
**Supplementary Figure 23.** Li ion transference number of PP, anatase TiO<sub>2</sub>/PP, GO/PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators with different surface area mass loadings. Error bars were included, which represent the standard deviation of the data taken from five samples.



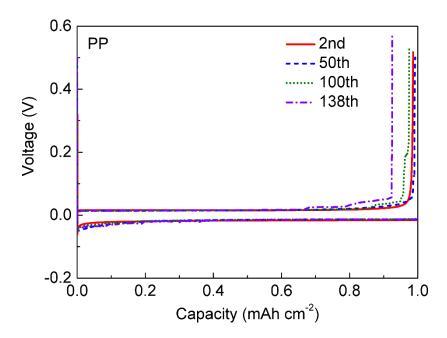
**Supplementary Figure 24.** Voltage profiles of Li plating/stripping processes in Li||Cu cells with an areal capacity of 1 mAh cm $^{-2}$  at 1 mA cm $^{-2}$ .



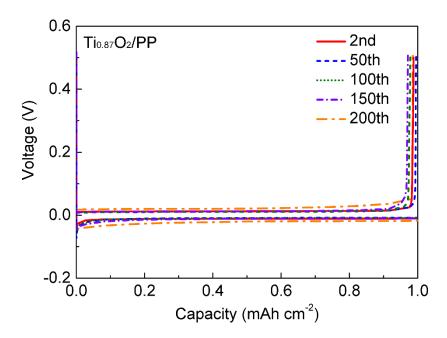
**Supplementary Figure 25.** Voltage profiles of Li plating/stripping processes in Li||Cu cells with GO/PP separators with an areal capacity of 1 mAh cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>.



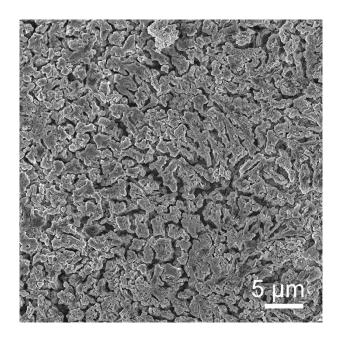
Supplementary Figure 26. Coulombic efficiencies of Na $\parallel$ Cu cells with PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators with an area capacity of 1 mAh cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>.



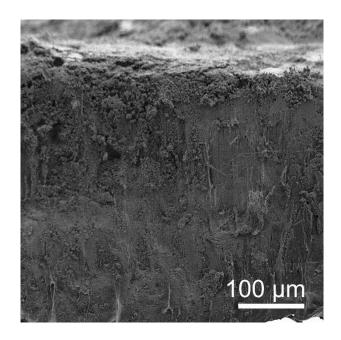
**Supplementary Figure 27.** Voltage profiles of Na plating/stripping processes in Na||Cu cells with PP separators with an areal capacity of 1 mAh cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>.



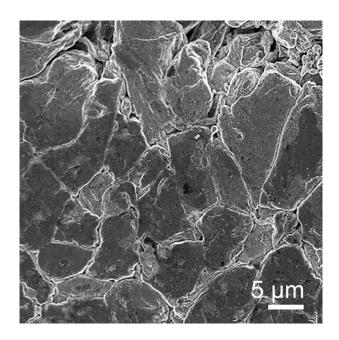
**Supplementary Figure 28.** Voltage profiles of Na plating/stripping processes in Na||Cu cells with  $Ti_{0.87}O_2/PP$  separators with an areal capacity of 1 mAh cm<sup>-2</sup> at 1 mA cm<sup>-2</sup>.



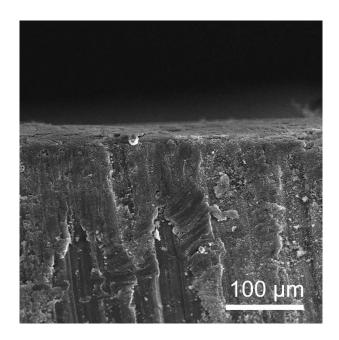
**Supplementary Figure 29.** SEM image of the Li metal anodes disassembled from the symmetrical cell with the PP separator at a current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for 20 cycles.



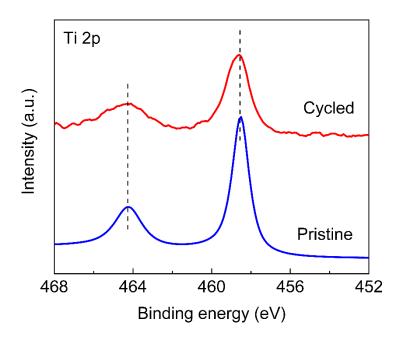
**Supplementary Figure 30.** Cross-section SEM image of the Li metal anodes disassembled from the symmetrical cell with the PP separator at a current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for 20 cycles.



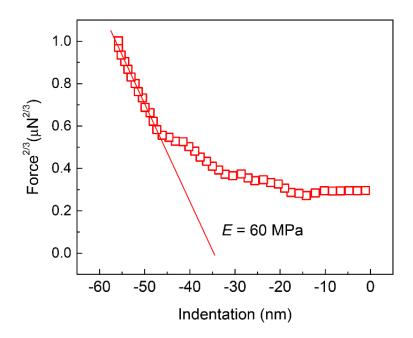
**Supplementary Figure 31.** SEM image of the Li metal anodes disassembled from the symmetrical cell with the  $Ti_{0.87}O_2/PP$  separator at a current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for 20 cycles.



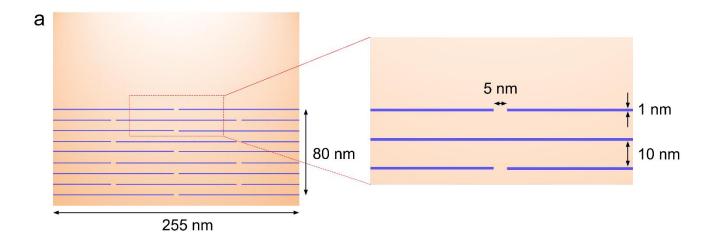
Supplementary Figure 32. Cross-section SEM image of the Li metal anodes disassembled from the symmetrical cell with the  $Ti_{0.87}O_2/PP$  separator at a current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for 20 cycles.

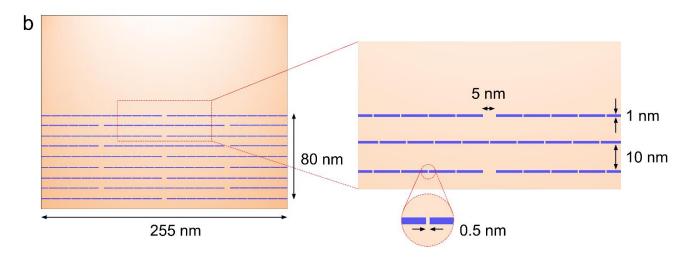


Supplementary Figure 33. High-resolution XPS spectrum of Ti 2p of pristine and cycled  $Ti_{0.87}O_2/PP$  separators disassembled from the symmetrical cell at a current density of 2 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> for 20 cycles.

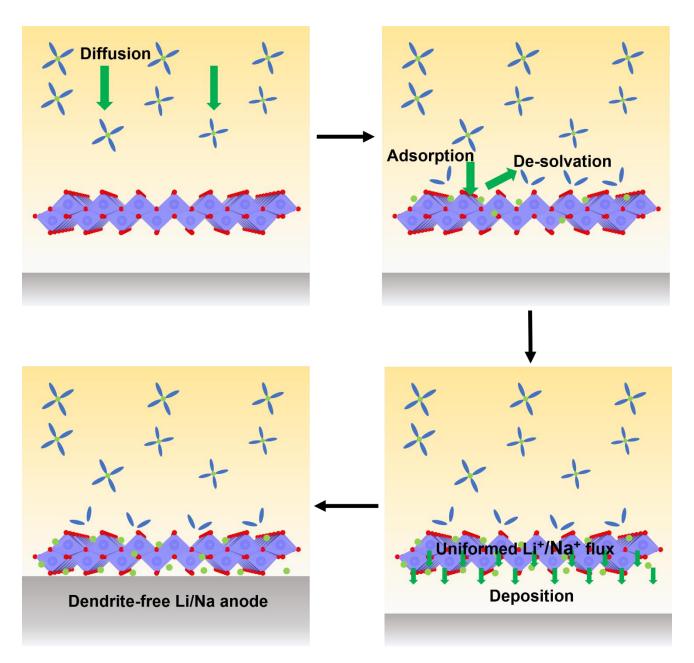


**Supplementary Figure 34.** A representative force-indentation curve of the Ti<sub>0.87</sub>O<sub>2</sub>/PP separator. The curve is fitted using the Hertzian model in the linear region.

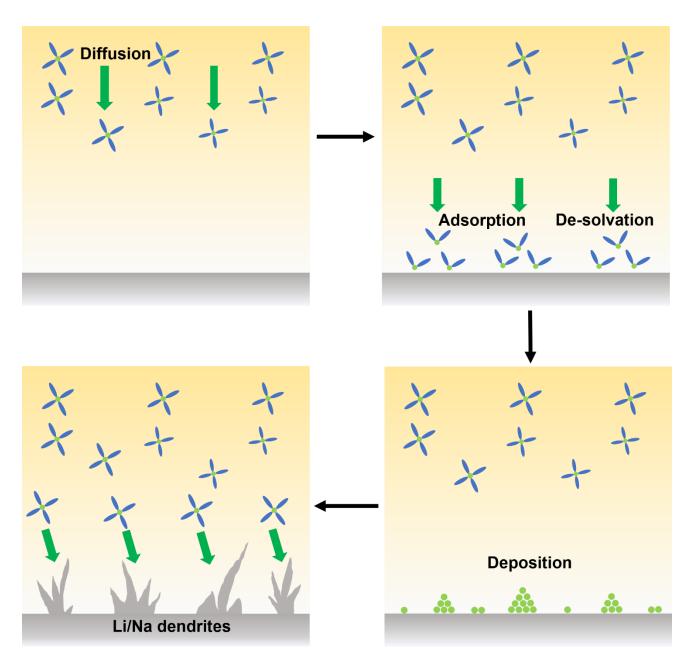




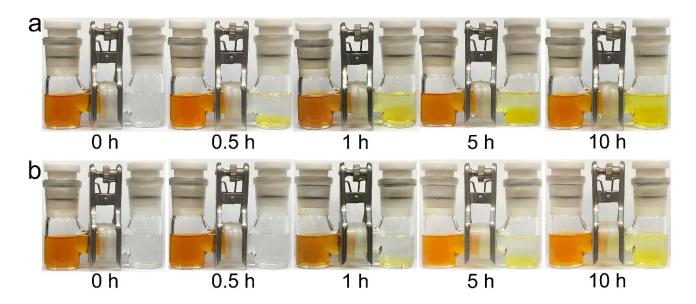
**Supplementary Figure 35.** The models of restacked thin layers for the (a) conventional nanosheets (without defects) and (b) defective nanosheets.



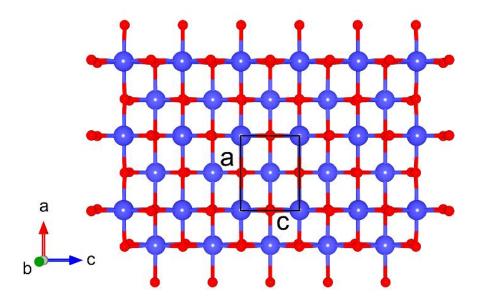
**Supplementary Figure 36.** Schematic illustration of mechanism of dendrite-free Li/Na anode by using anionic  $Ti_{0.87}O_2$  nanosheets with atomic Ti vacancies.



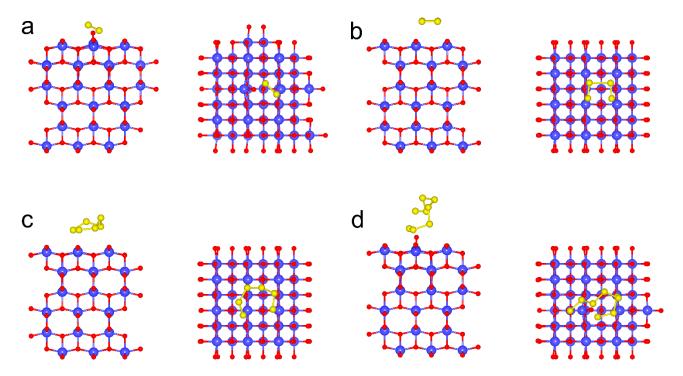
**Supplementary Figure 37.** Schematic illustration of Li/Na deposition over the bare anode.



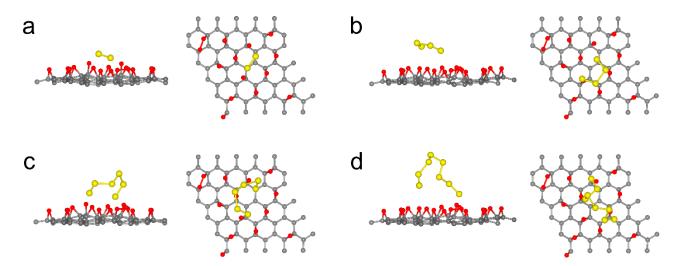
**Supplementary Figure 38.** Polysulfide permeation measurements in H-type cells with the (a) anatase TiO<sub>2</sub>/PP and (b) GO/PP separators.



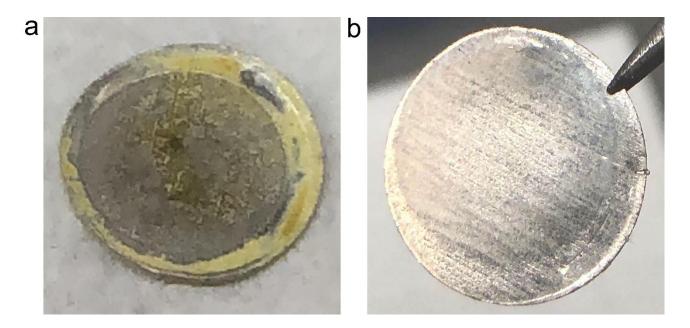
**Supplementary Figure 39.** Calculation of negative charge density of Ti<sub>0.87</sub>O<sub>2</sub><sup>0.52-</sup> nanosheets. In-plane structure of Ti<sub>0.87</sub>O<sub>2</sub> shows a rectangular unit cell with a = 0.38 nm and c = 0.30 nm. The 2D charge density ( $\rho$ ) of Ti<sub>0.87</sub>O<sub>2</sub> can be calculated based on the in-plane unit cell area,  $\rho_{\text{(Ti0.87O2)}} = 2 \times 0.52 \times 1.60 \times 10^{-19} / (a \times c) = 1.46 \text{ C m}^{-2}$ .



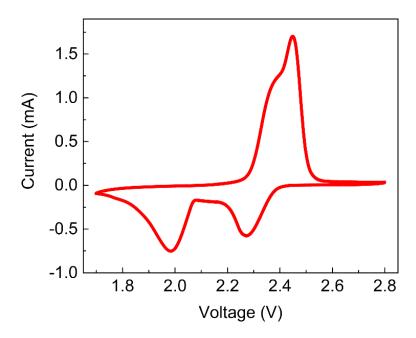
**Supplementary Figure 40.** Optimized conformations of (a)  $S_2^{2-}$ , (b)  $S_4^{2-}$ , (c)  $S_6^{2-}$  and (d)  $S_8^{2-}$  on anatase  $TiO_2$ .



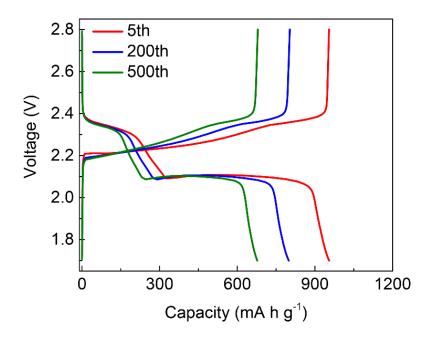
**Supplementary Figure 41.** Optimized conformations of (a)  $S_2^{2^-}$ , (b)  $S_4^{2^-}$ , (c)  $S_6^{2^-}$  and (d)  $S_8^{2^-}$  on GO sheet.



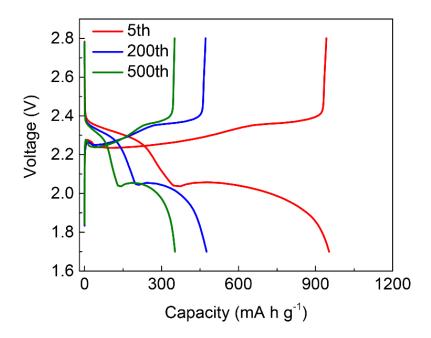
Supplementary Figure 42. Digital images of the Li metal anodes of the disassembled cells after 10 cycles with the (a) PP and (b)  $Ti_{0.87}O_2/PP$  separators.



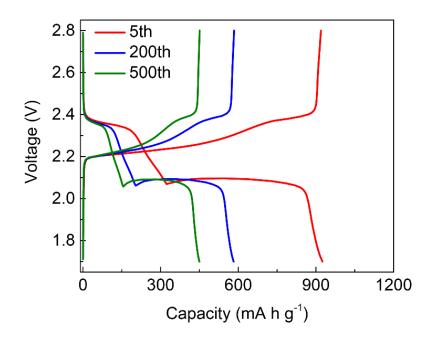
Supplementary Figure 43. CV curve of the Li–S cell with a  $Ti_{0.87}O_2/PP$  separator at 0.1 mV s<sup>-1</sup>.



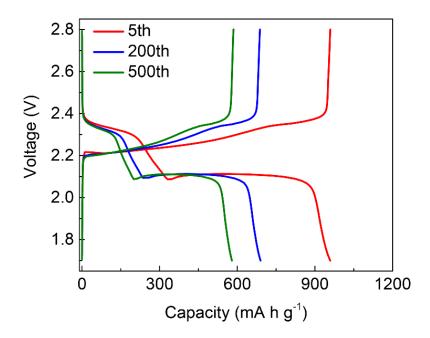
Supplementary Figure 44. Voltage profiles of the Li-S cell with a Ti<sub>0.87</sub>O<sub>2</sub>/PP separator at 0.2C.



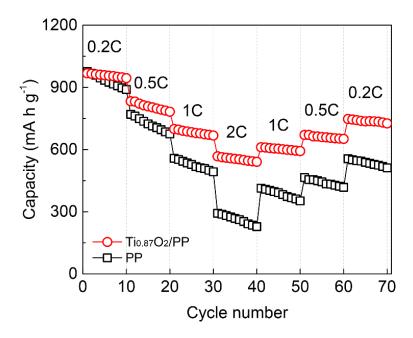
**Supplementary Figure 45.** Voltage profiles of the Li–S cell with a PP separator at 0.2C.



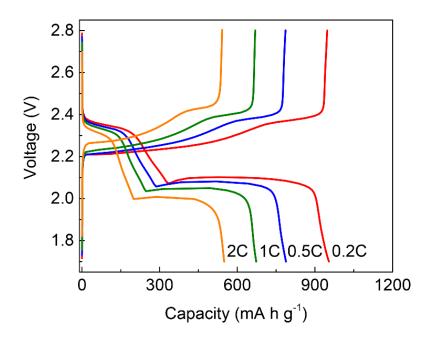
Supplementary Figure 46. Voltage profiles of the Li–S cell with an anatase  $TiO_2/PP$  separator at 0.2C.



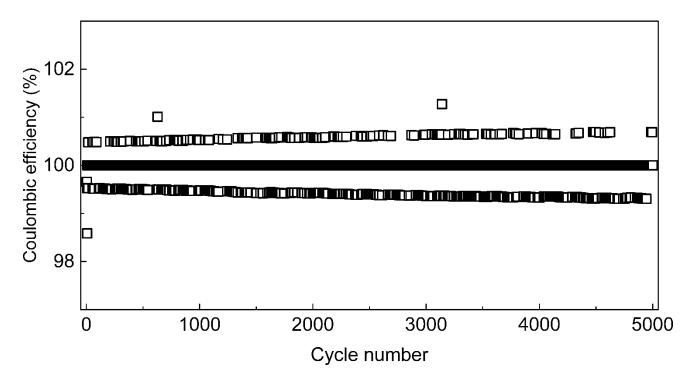
**Supplementary Figure 47.** Voltage profiles of the Li–S cell with a GO/PP separator at 0.2C.



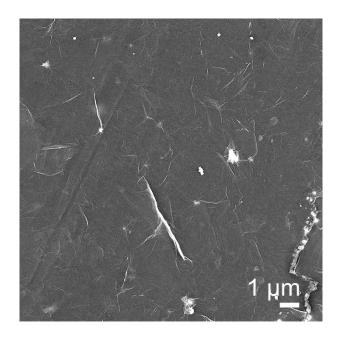
**Supplementary Figure 48.** The rate performance of Li–S cells with PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators.



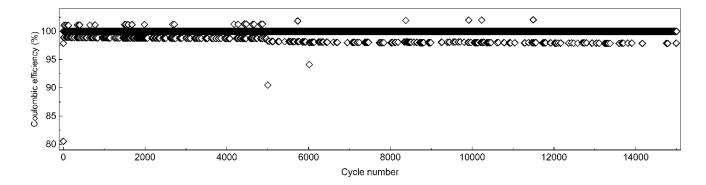
**Supplementary Figure 49.** Voltage profiles of the Li–S cell with a Ti<sub>0.87</sub>O<sub>2</sub>/PP separator at various C rates.



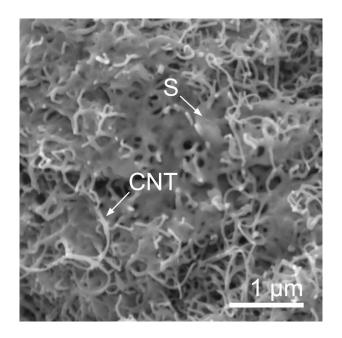
Supplementary Figure 50. Coulombic efficiency for a Li-S cell with a  $Ti_{0.87}O_2/PP$  separator during the long-term cycling at 1C for 5000 cycles.



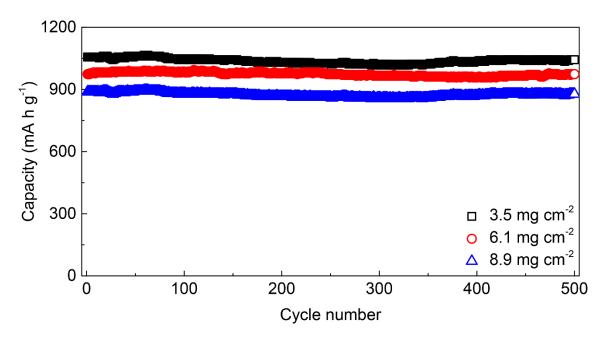
**Supplementary Figure 51.** SEM image of the cycled Ti<sub>0.87</sub>O<sub>2</sub>/PP separators from the disassembled cells in a fully discharged state after 500 cycles.



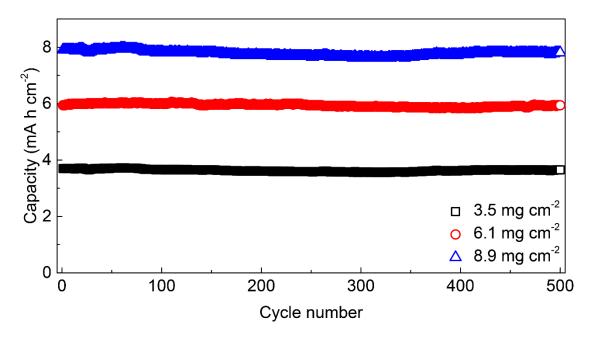
Supplementary Figure 52. Coulombic efficiency for a Li-S cell with a  $Ti_{0.87}O_2/PP$  separator at a sulfur mass loading of 3.5 mg cm<sup>-2</sup> during the long-term cycling.



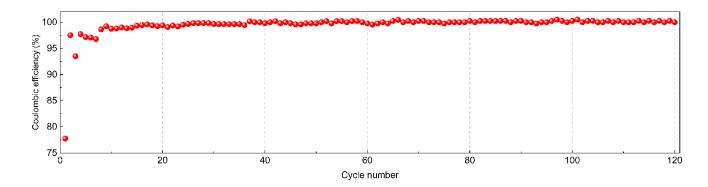
**Supplementary Figure 53.** SEM image of the CNT/S cathodes.



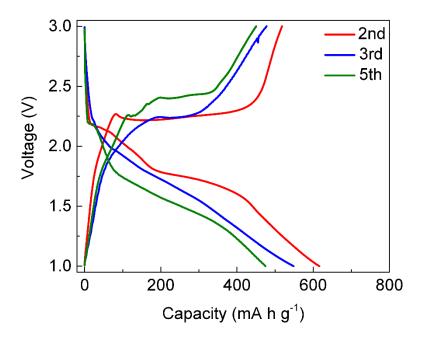
Supplementary Figure 54. Cycling performance of the Li-S cells at 0.2C using the CNT/S cathodes and the  $Ti_{0.87}O_2/PP$  separators.



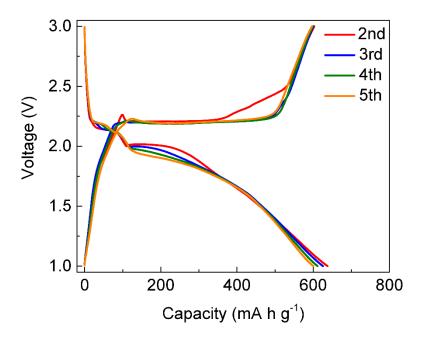
Supplementary Figure 55. Areal capacities of the Li-S cells using the CNT/S cathodes and the  $Ti_{0.87}O_2/PP$  separators.



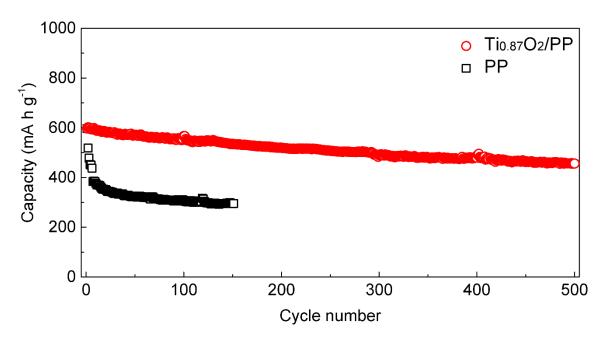
Supplementary Figure 56. Coulombic efficiency for a flexible Li-S pouch cell with a  $Ti_{0.87}O_2/PP$  separator under different bending angles during the cycling test.



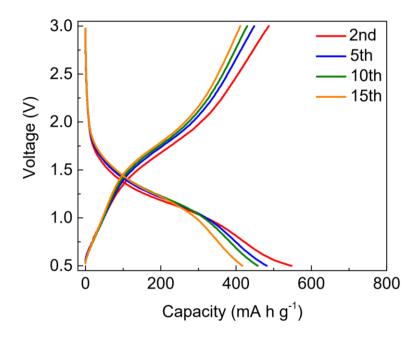
**Supplementary Figure 57.** Voltage profiles of the Li–Se cell with a PP separator at 0.2C.



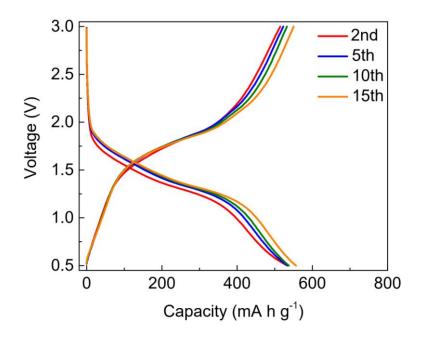
Supplementary Figure 58. Voltage profiles of the Li–Se cell with a  $Ti_{0.87}O_2/PP$  separator at 0.2C.



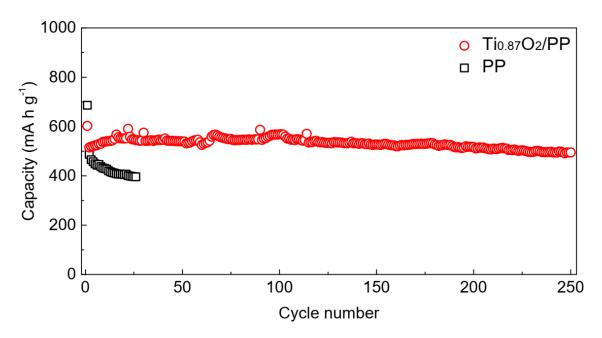
**Supplementary Figure 59.** Cycling performance of the Li-Se cells at 0.2C with PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators.



**Supplementary Figure 60.** Voltage profiles of the Na–Se cell with a PP separator at 0.2C.



Supplementary Figure 61. Voltage profiles of the Na–Se cell with a Ti<sub>0.87</sub>O<sub>2</sub>/PP separator at 0.2C.



**Supplementary Figure 62.** Cycling performance of the Na-Se cells at 0.2C with PP and Ti<sub>0.87</sub>O<sub>2</sub>/PP separators.

Supplementary Movie 1. Molecular dynamic simulation of the diffusion of polysulfide anions and Li ions through the anionic  $Ti_{0.87}O_2$  monolayer with one Ti vacancy.

Supplementary Table 1. Electrochemical properties of various functional separators in Li-S cells.

| Functional separators                     |                                                  |                   | Battery performance               |                               |                      |                                                                       |                                                                                           |     |
|-------------------------------------------|--------------------------------------------------|-------------------|-----------------------------------|-------------------------------|----------------------|-----------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-----|
| Materials                                 | Surface area mass loading (mg cm <sup>-2</sup> ) | Thickness<br>(μm) | Cathode composite active material | S wt.% (mg cm <sup>-2</sup> ) | Voltage<br>range (V) | Electrolyte                                                           | Cycling performance (cycles, C-rates (1C= 1675 mA g <sup>-1</sup> ), capacity decay rate) | Ref |
| GO                                        | 0.12                                             | 5                 | Carbon<br>black/S                 | 1.0-1.5                       | 1.5-3.0              | 1 M LiTFSI in  DOL/DME  (v/v = 1:1)                                   | 100, 0.1C, 0.23%                                                                          | 1   |
| Nafion/GO                                 | 0.128                                            | 0.030             | Garphene/<br>CNT/S                | 1.2                           | 1.5-3.0              | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$                                  | 200, 0.1C, 0.18%                                                                          | 2   |
| Commercial graphene                       | 1.3                                              | 30                | Carbon<br>black/S                 | 1.5-2.1                       | 1.5-2.8              | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with 1.0 wt% $LiNO_3$ | 500, 0.9C, 0.064%                                                                         | 3   |
| CVD-<br>derived<br>porous<br>graphene     | 0.54                                             | 10                | CNT/S                             | 1.8–2.0                       | 1.8-2.8              | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with 1.0 wt% $LiNO_3$ | 150, 0.5C, 0.16%                                                                          | 4   |
| Commercial graphene@ porous carbon (G@PC) | 0.075                                            | 0.9               | Carbon<br>black/S                 | 3.5                           | 1.6-2.8              | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 2.0 wt%  LiNO <sub>3</sub>  | 100, 0.2C, 0.08%                                                                          | 5   |

| Co/N-<br>carbon<br>sheets/reduc<br>ed graphene<br>oxide | 0.2     | 41.3  | CNT/S             | 1.0       | 1.7-2.8 | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with 1.0 wt% $LiNO_3$         | 500, 0.2C, 0.07%     | 6  |
|---------------------------------------------------------|---------|-------|-------------------|-----------|---------|-------------------------------------------------------------------------------|----------------------|----|
| Cellular CVD- derived graphene framework                | 0.3     | 30    | CNT/S             | 1.2       | 1.7-2.8 | 1 M LiTFSI in DOL/DME (v/v = 1:1)                                             | 300, 0.8375C, 0.085% | 7  |
| B-rGO                                                   | 0.2-0.3 | 25    | CNT/S             | 1.45-1.56 | 1.8-2.8 | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with $0.2 \text{ M}$ $LiNO_3$ | 300, 0.1C, 0.1532%   | 8  |
| rGO@sodiu m lignosulfona te (rGO@SL)                    | 0.2     | ~20   | Carbon<br>black/S | 1.5       | 1.7-2.7 | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with 1.0 wt% $LiNO_3$         | 1000, 2C, 0.026%     | 9  |
| CNTs/N-doped carbon quantum dot (CNT/NCQ D)             | 0.15    | 25~30 | Carbon<br>black/S | 1.3-1.5   | 1.8-2.7 | $1 \text{ M LiTFSI in}$ $DOL/DME$ $(v/v = 1:1)$ with 2.0 wt% $LiNO_3$         | 1000, 0.5C, 0.05%    | 10 |
| CNF-Gum<br>Arabic                                       | 0.25    | 19    | CNF/S             | 1.1       | 1.7-2.8 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$                                           | 250, 1C, 0.024%      | 11 |

|                                                      |       |           |                   |         |         | with 2.0 wt% LiNO <sub>3</sub>                                               |                   |    |
|------------------------------------------------------|-------|-----------|-------------------|---------|---------|------------------------------------------------------------------------------|-------------------|----|
| Mg <sub>2</sub> Al-<br>LDH                           | 0.018 | 0.02-0.03 | Carbon<br>black/S | 1.2-1.4 | 1.7-2.8 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$ with 1.0 wt% LiNO <sub>3</sub>           | 200, 0.5C, 0.18%  | 12 |
| NiFe-<br>LDH/CVD-<br>derived N-<br>doped<br>graphene | 0.3   | 1.5       | Carbon/S          | 1.2     | 1.7-2.8 | 1 M LiTFSI in<br>2.5 M<br>$\text{Li}_2\text{S}_8/\text{tetragly}$ me         | 1000, 2C, 0.06%   | 13 |
| $MoS_2$                                              | -     | 0.350     | Carbon<br>black/S | -       | 1.5-3.0 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1)  with 1.0 wt%  LiNO <sub>3</sub>         | 600, 0.5C, 0.083% | 14 |
| MoS <sub>2</sub> - PDDA/PAA                          | 0.1   | 3         | Carbon<br>black/S | 1.2-4.0 | 1.7-2.6 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$ with 1.0 wt% LiNO <sub>3</sub>           | 2000, 1C, 0.029%  | 15 |
| Co <sub>9</sub> S <sub>8</sub>                       | 0.16  | -         | Carbon<br>black/S | 2.0     | 1.8-2.8 | 1.85 M $LiCF_3SO_3 \text{ in}$ $DOL/DME$ $(v/v = 1:1)$ $with 0.1 M$ $LiNO_3$ | 1000, 1C, 0.039%  | 16 |

| Sb <sub>2</sub> Se <sub>3</sub> . <sub>x</sub> /rGO | 0.5       | 32    | Carbon<br>black/S | 1.8     | 1.7-2.8 | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 1.0 wt%  LiNO <sub>3</sub>          | 500, 1C, 0.027%    | 17 |
|-----------------------------------------------------|-----------|-------|-------------------|---------|---------|-------------------------------------------------------------------------------|--------------------|----|
| MoP/rGO                                             | 0.35-0.45 | 10    | Carbon/S          | 3.6-4.0 | 1.8-2.8 | $0.6 \text{ M LiTFSI}$ in DOL/DME $(v/v = 1:1)$ with $0.4 \text{ M}$ $LiNO_3$ | 120, 0.1C, 0.045%  | 18 |
| Ti <sub>3</sub> C <sub>2</sub> MXene                | 0.1       | 0.522 | Carbon<br>black/S | 1.2     | 1.7-2.8 | 1  M LiTFSI in  DOL/DME $(v/v = 1:1)$ with $0.1  M$ LiNO <sub>3</sub>         | 500, 0.5C 0.062%   | 19 |
| Black<br>Phosphorus                                 | 0.4       | ~0.35 | Carbon<br>black/S | 1.5–2   | 1.7-2.6 | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 1.0 wt%  LiNO <sub>3</sub>          | 100, 0.2C, 0.14%   | 20 |
| Super P/Red phosphorus                              | 0.3       | 8     | Carbon<br>black/S | 2       | 1.5-3.0 | 1  M LiTFSI in  DOL/DME $(v/v = 1:1)$ with $0.1  M$ LiNO <sub>3</sub>         | 500, 1C, 0.036%    | 21 |
| BN-carbon                                           | -         | 6~7   | Carbon<br>black/S | 2.1     | 1.5-3.0 | 1 M LiPF <sub>6</sub> in<br>EC/DEC (v/v = 1:1)                                | 250, 0.5C, 0.0936% | 22 |

| BaTiO <sub>3</sub>                                                                        | 2.4   | 18-23 | Carbon<br>black/S | 3.2     | 1.8-2.6 | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 0.3 M  LiNO <sub>3</sub>   | 50, 0.1C, 0.34%  | 23 |
|-------------------------------------------------------------------------------------------|-------|-------|-------------------|---------|---------|----------------------------------------------------------------------|------------------|----|
| H <sub>x</sub> MnO <sub>2+x</sub> /l<br>iquid phase-<br>exfoliated<br>graphene/C<br>NTs   | 0.2   | 3     | CNT/S             | 1.8     | 1.7-2.8 | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 1.0 wt%  LiNO <sub>3</sub> | 1000, 1C, 0.04%  | 24 |
| TiO <sub>2</sub> /comm<br>ercial<br>graphene                                              | 0.15  | 3     | CNT/S             | 1.2     | 1.8-2.8 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$ with 1.0 wt% LiNO <sub>3</sub>   | 300, 0.5C, 0.01% | 25 |
| Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /ch<br>emically<br>exfoliated<br>graphene | 0.346 | 35    | Carbon<br>black/S | 1.0-1.2 | 1.7-2.8 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$ with 1.0 wt% LiNO <sub>3</sub>   | 500, 1C, 0.028%  | 26 |
| Ni <sub>3</sub> (HITP) <sub>2</sub>                                                       | 0.066 | 0.34  | CNT/S             | 8       | 1.7-2.8 | 1 M LiTFSI in DOL/DME $(v/v = 1:1)$ with 2.0 wt% LiNO <sub>3</sub>   | 500, 1C, 0.066%  | 27 |
| Cu <sub>2</sub> (CuTCP<br>P)<br>nanosheets                                                | 0.1   | 0.5   | Carbon<br>black/S | 2       | 1.7-2.8 | 1 M LiTFSI in  DOL/DME $(v/v = 1:1)$ with 2.0 wt%                    | 900, 1C, 0.032%  | 28 |

LiNO<sub>3</sub>

| CNT@ZIF-                                      | 0.9  | 15  | Carbon<br>black/S | 1.2     | 1.5-3.0 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1) 100, 0.2C, 0.45%  with 0.2 M  LiNO <sub>3</sub>   | 29 |
|-----------------------------------------------|------|-----|-------------------|---------|---------|---------------------------------------------------------------------------------------|----|
| Ce-<br>MOF/CNT                                | 0.4  | 8   | Carbon<br>black/S | 2.5     | 1.7-2.8 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1) 800, 1C, 0.022%  with 0.1 M  LiNO <sub>3</sub>    | 30 |
| MOF@PV<br>DF-HFP                              | None | 28  | Carbon<br>cloth/S | 1-1.5   | 1.5-3.0 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1) 600, 0.5C, 0.0549%  with 0.1 M  LiNO <sub>3</sub> | 31 |
| Bacterial cellulose/2 D MOF-Co (BC/2D MOF-Co) | 2.53 | 25  | Carbon<br>black/S | 1.5     | 1.7-2.8 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1) 600, 1C, 0.07%  with 1.0 wt%  LiNO <sub>3</sub>   | 32 |
| MOF@GO                                        | 0.3  | ~10 | CMK3/S            | 0.6-0.8 | 1.5-3.0 | 1 M LiTFSI in  DOL/DME  (v/v = 1:1) 1500, 1C, 0.019%  with 0.1 M  LiNO <sub>3</sub>   | 33 |

|                                   |       |       |         |         |         | 1 M LiTFSI in                   |      |
|-----------------------------------|-------|-------|---------|---------|---------|---------------------------------|------|
| Lamanita                          |       |       | Carbon  |         |         | DOL/DME                         |      |
| Laponite                          | 0.7   | 3.5   |         | 1.0-1.2 | 1.7-2.8 | (v/v = 1:1) 500, 0.2C, 0.06%    | 34   |
| nanosheets                        |       |       | black/S |         |         | with 0.2 M                      |      |
|                                   |       |       |         |         |         | LiNO <sub>3</sub>               |      |
|                                   |       |       |         | 1.5     |         | 1 M LiTFSI in 5000, 1C, 0.0036% |      |
| т: О                              |       |       | Carbon  |         |         | DOL/DME                         | This |
| Ti <sub>0.87</sub> O <sub>2</sub> | 0.016 | 0.080 |         | 2.5     | 1.7-2.8 | (v/v = 1:1) 4900, 1C, 0.0035%   | work |
| nanosheets                        |       |       | black/S | 3.5     |         | with 1.0 wt% 10000, 2C, 0.0035% | WOLK |
|                                   |       |       |         |         |         | LiNO <sub>3</sub>               |      |

 $\textbf{Supplementary Table 2.} \ \ Comparison \ of \ \ Li^{\scriptscriptstyle +} \ conductivities \ of \ pristine \ and \ modified \ separators.$ 

| M. J.C. J                             | Li <sup>+</sup> conductivity | Pristine  | Li <sup>+</sup> conductivity | D.£       |
|---------------------------------------|------------------------------|-----------|------------------------------|-----------|
| Modified separator                    | mS cm <sup>-1</sup>          | separator | mS cm <sup>-1</sup>          | Ref       |
| MoS <sub>2</sub> /Celgard             | 0.20                         | Celgard   | 0.33                         | 14        |
| LNS/CB-Celgard                        | 0.590                        | Celgard   | 0.559                        | 34        |
| MOF@PVDF-HFP                          | 0.094                        | Celgard   | 0.138                        | 31        |
| MoS <sub>2</sub> -PDDA/PAA            | 0.48                         | Celgard   | 0.51                         | 15        |
| Co-N <sub>x</sub> @NPC/G-PP           | 0.684                        | PP        | 0.403                        | 6         |
| Ti <sub>0.87</sub> O <sub>2</sub> /PP | $0.381 \pm 0.028$            | PP        | $0.305 \pm 0.015$            | This work |

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